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Behavior of disinfection by-products in a drinking water distribution system

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ABSTRACT

This research was to study the temporal and spatial variations of disinfection by-products (DBPs) in a full-scale drinking water system that applied a regular chlorine disinfection strategy. The analysis of collected water samples showed that trichloromethane (TCM), chloral hydrate (CH), trichloroacetic acid (TCAA), and drichloroacetic acid (DCAA) were the main DBPs in this system. Statistically significant differences ($P < 0.05$) of DBPs were observed among four seasons, with higher average levels of DBPs occurred during fall and winter. CH has a high risk of exceeding the standard. TCM levels increased and stabilized in the extremities of the distribution system, whereas CH, TCAA, and DCAA levels in the system began to increase and then decreased with the extension of contacted time. CH levels increased about 1.5 times after 24 h contact in the distribution system. The temporal and spatial variation of each disinfection by-product (DBP) were not consistent. In this system, permanganate index (COD_{Mn}) and chromaticity were the main parameters for explaining the fate of CH. TCM level cannot serve as a good indicator for CH generation. TCM was the only type of DBPs that had a moderate correlation with rainfall (lag 2 months, $r = 0.487$). Granular active carbon secondary filtration can effectively intercept part of DBPs precursors in water, which can reduce CH concentration by 32.7 % on average.

Keywords: Drinking water; Disinfection by-products; Chloral hydrate; Seasonal variations; Spatial variations; Water distribution system

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1. Introduction

Ensuring the safety of drinking water by eliminating water-borne microbial pathogens that cause typhoid fever, cholera, and gastroenteritis through disinfection is a major public achievement [1]. The disinfectant interacted with natural organic matter (NOM) in the source water, forming a series of unexpected chemicals collectively called disinfection by-products (DBPs) [2].

Haloacetaldehydes (HALs) are considered as the third-largest group of identified DBPs by weight in drinking water, ranked after trihalomethanes (THMs) and haloacetic acids (HAAs) [3]. In recent years, toxicologists linked the toxicity of HALs to effects on human health. The cytotoxicity and genotoxicity of HALs were compared with five other types of DBPs including THMs and HAAs, and the results indicated that HALs is the second most cytotoxic DBPs class [4]. The most prevalent halogenated acetaldehyde (HAL) is chloral hydrate (CH), which is considered as regular DBPs in many countries [5].

Extremely high CH levels (i.e., 263 μg/L) have been tested in the Canadian drinking water system, which is higher than the maximum acceptable level (10 μg/L) [6]. In the distribution system, the occurrence variability of CH in chlorinated water might be influenced significantly by season and geographical location [2]. These temporal and spatial variations are associated with the quality of the water source and the operations conducted in the treatment plant [7]. Additionally, regional climate and operational parameters (e.g., temperature, precipitation, and disinfectant dose) vary with seasons, therefore, the

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difficulties to fully grasp the variations need to be considered [8]. The long sampling intervals and low sampling frequencies (4 times per year) of drinking water can reduce the statistical significance of observing the temporal and spatial variations of DBPs [2].

The occurrence and variation of DBPs have been observed to be influenced by some of measurable parameters (e.g., bromide, iodide, pH, and temperature) as well as seasonal and climatic factors [3]. The operational parameters of the drinking water system, including the filtration methods used in the removal of natural organic materials (NOM), water residence time, and the disinfection strategies within the distribution system, can have great effects on DBPs occurrence [3]. Moreover, the studies on the main factors affecting the temporal and spatial variations of DBPs, which include drinking water treatment plant (DWTP) operation parameters, raw water quality parameters, and climatic conditions around the raw water area have not attracted widespread attention. Very few DWTPs will seek effective measures to control the occurrence and variation of DBPs in the drinking water system because of these main influence factors [1].

In this paper, the temporal and spatial variations of DBPs in the treated water of one large-size utility in Harbin City (China) were studied. Particularly, the impact on the requirements of current and future regulations by seasonal, intra-seasonal, and spatial variations of DBPs was focused on. The factors (i.e., water quality, operational parameters, and climatic conditions) were identified, which might be responsible for these variations. Also, this study suggested effective strategies to control the formation of CH in the drinking water system with bench-scale chlorine contact disinfection experiments.

2. Methodology

2.1. Case study

Pingfang DWTP was selected for this study. DWTP locates in Harbin (a city in northeastern China), with a designed production of 900,000 m^3/d. The raw water was drawn from surface water and stored in Mopanshan Reservoir which is 180 km away from DWPT. Raw water has the property of low temperature and low turbidity. The water treatment process at DWTP is depicted in Fig. 1. A conventional treatment train (as followed) has been adopted: coagulation–flocculation, sedimentation, filtration, and disinfection with sodium hypochlorite. The treated water was remained in the chlorine-contact reservoir for at least 5 h. There was no secondary chlorination equipment within the distribution system. DWPT only adds disinfectants in filtrated water to ensure that there is residual chlorine downstream of the system. The studied distribution system was a gravity flow line that was mainly made of ductile iron, the total contact time between treated water and residual chlorine in the pipeline was 72 h.

2.2. Sampling strategy and laboratory analysis

Fig. 1 presents the nomenclature of the sampling points. An intensive 48 month sampling campaign was conducted from January 2016 to December 2019. Samples were collected monthly at representative points, from raw water to the extremities of the distribution system. In the distribution system of DWTP in Fig. S1, point DW 6, DW 12, DW 24, DW 36, DW 48, and DW 72, respectively, represent the locations that increase with water residence time (*t* = 6, 12, 24, 36, 48,

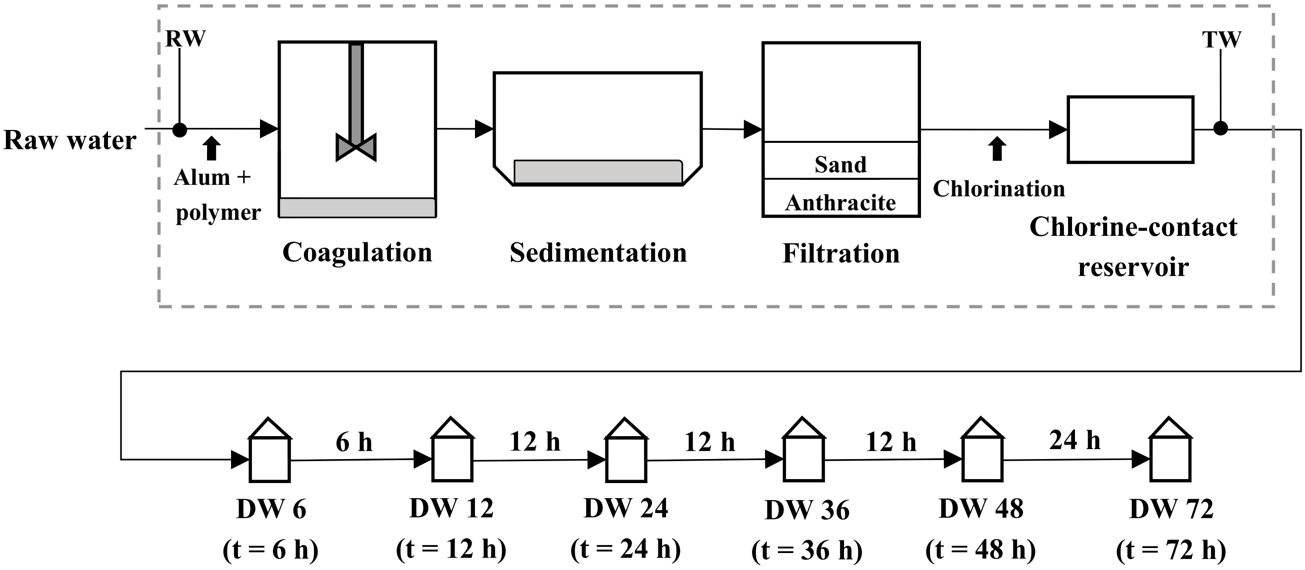

Fig. 1. Schematic diagrams of DWTP, and the sampling points within the plants (in the rectangle) or along with the distribution system (outside the rectangle). The abbreviations are as follows. RW: raw water, TW: treated water, DW: distributed water. For sampling points in the distribution system, the contact time (*t*) of treated water and residual chlorine from plant exit to sampling point were indicated in parentheses, the contact time between different sampling points were indicated above the arrows.

and 72 h, respectively). The concentrations of bromide and DBPs in the raw water are the main parameters to characterize the occurrence and variation of DBPs in treated and distributed water. All the samples from the different sampling points were carried DBPs, water temperature, pH, turbidity, permanganate index (COD_{Mn}), and chromaticity determinations. Chlorine residuals (free) were determined only at the points after chlorination. Water samples were collected in 300 mL glass bottles with ground-glass stoppers. 1.5 mL sodium thiosulfate solution (10%) was added to 50 mL amber vials to remove chlorine residuals before sampling and to prevent any additional DBPs formation before quantitative measurement. 250 mL plastic bottles were used for the analysis of COD_{Mn}. The collected samples were carefully stored in the dark at 4°C (within 7 d) and carried to the laboratory for analysis.

The analysis of COD_{Mn} was referred as the oxygen consumption detection method [9]. Chromaticity could be measured with visual colorimetry. Ion chromatography was used for the analysis of bromide, but in all cases, measurements were below the method quantification limits (MQLs) (15 μg/L). The measurement of free chlorine residual was conducted on-site using the DPD colorimetric method (Standard method 4500-Cl-G) with a DR900 colorimeter from Hach [3]. Temperature, pH, turbidity, and chlorine dose was monitored by the utility with their routine online water quality and operational control system.

Liquid–liquid extraction (LLE) using methyl-*tert*-butyl-ether (MTBE) based on USEPA Method 551.1 was used for the determination of trichloromethane (TCM) and CH [9]. The measurement of the extract was conducted on a Perkin Elmer dual-column gas chromatography combined with electron capture detection (Clarus 500 dual-column GC/ECD, Perkin Elmer Instruments Co. Ltd., Shanghai). Trichloroacetic acid (TCAA) and drichloroacetic acid (DCAA) were determined using the micro-LLE gas chromatographic method based on USEPA Method 552.2 [10]. The MQLs of DBPs in this paper are listed in Table 1. All results below the MQLs were considered equal to zero.

2.3. Statistical analysis

Before further statistical tests, Shapiro–Wilk test was used to ensure if the distribution was normal. All the datasets studied in this paper did not represent a normal distribution. For data with non-normal distribution, the comparison of two mean values was shown by Mann–Whitney *U*-test. Kruskal–Wallis *H*-test was applied to compare more than two mean values. When the statistical significance level (*P*) was no more than 0.05, the difference was statistically significant. After the statistical test of more than two mean values, Tukey's multiple comparison test was conducted based on a significance level of 0.05 to determine which average was statistically different. Spearman correlation analysis was performed at the significance level of 0.01 or 0.05 to evaluate the linear relationship and correlation coefficient (*r*) between DBPs and other parameters. All these analyses were performed using SPSS statistics software (version 23.0).

Table 1
Method quantification limits (MQLs) for DBPs

DBPs	Abbreviations	MQLs (μg/L)
Trichloromethane	TCM	0.32
Chloral hydrate	CH	0.41
Trichloroacetic acid	TCAA	0.34
Dichloroacetic acid	DCAA	0.20

2.4. Bench-scale hydrolysis and chlorine contact disinfection experiments

Amber glass bottles of 2.5 L were used for the performance of bench-scale chlorination tests. Sand filtered water from DWTP and Haxi drinking water treatment plant (HWTP) were selected in this paper. HWTP treating an average of 200,000 m^3 of water a day from Songhua River in Harbin. Both DWTP and HWTP apply the same utilities before the disinfection process. Granular active carbon (GAC) was soaked, washed, and dried before loading into the filter column (*D* = 50 mm, *H* = 400 mm), with a 5 cm height of GAC. The GAC filtered water samples were collected after 10 min as the sand filtered water flow goes through the GAC filter column stably. Finally, four types of water samples were obtained ((a): DWTP sand filter effluent, (b): DWTP GAC filter effluent, (c): HWTP sand filter effluent, (d): HWTP GAC filter effluent). All water samples were filtered in advance with 0.45 μm glass fiber membranes. The phosphate buffer solution was used to control pH to 6.9.

3. Results and discussion

3.1. Water quality and operational parameters in DWTP

The main parameters for raw water and treated water from the utility during the studied period are presented in Table 2. The water source of the lake reservoir (Mopanshan Reservoir) is slow-flow water, which has a slow updating speed. Low COD_{Mn} (~3.49 μg/L), turbidity (~2.03 NTU), and chromaticity (~19.50) in raw water were observed in the flood season in spring when the water level rises in the reservoir area and thus is protected from pollution by the dilution of foreign pollutants. In contrast, high COD_{Mn} (~4.72 μg/L), turbidity (~2.58 NTU), and chromaticity (~26.12) were detected in raw water since a great amount of disinfection by-products formation potentials (DBPFPs) might be generated in the rainy season in fall, when the overland runoff, precipitation, and farmland irrigation led to a large number of foreign pollutants input into the reservoir region. The water quality characteristics of the reservoir might be affected by weather and farmland irrigation. Although the seasonal variation of COD_{Mn} in raw water did not change dramatically, the species composition and molecular magnitude of NOM in raw water might be different between seasons. This might result in different DBPs formation patterns. It is necessary to apply other indicators to analyze NOM characteristics in raw water in the future [10]. The parameters of the treated water are also variable with the season. The variation pattern of each parameter is basically consistent with that of raw water. The chlorine

Table 2
Average values for water quality and operational parameters in DWTP (standard deviations in parentheses)

Type of water	Parameters	Seasons[a]				Annual average (N = 48)	Maximum (N = 48)	Minimum (N = 48)
		Spring (N = 12)	Summer (N = 8)	Fall (N = 8)	Winter (N = 20)			
Raw water	Temperature (T, °C)	4.40 (3.20)	19.30 (1.80)	16.10 (3.10)	3.10 (2.30)	9.30 (8.33)	20.30	2.30
	pH	7.02 (0.22)	6.85 (0.23)	6.98 (0.16)	6.96 (0.13)	6.96 (0.18)	7.40	0.18
	COD_{Mn} (mg/L)	3.49 (0.59)	4.21 (1.53)	4.72 (0.70)	4.01 (0.67)	4.03 (0.90)	6.32	2.16
	Chromaticity	19.50 (7.05)	20.75 (8.15)	26.12 (5.28)	20.95 (3.03)	21.42 (5.56)	40.00	12.00
	Turbidity (NTU)	2.03 (1.74)	1.38 (0.76)	2.58 (1.94)	1.23 (1.07)	1.68 (1.41)	6.96	0.49
	Bromide (μg/L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Treated water	Temperature (T, °C)	8.12 (2.38)	17.58 (2.12)	16.75 (2.02)	7.56 (2.84)	10.90 (5.04)	21.00	3.90
	pH	6.86 (0.11)	6.80 (0.076)	6.78 (0.13)	6.85 (0.098)	6.84 (0.10)	7.08	6.50
	COD_{Mn} (mg/L)	1.27 (0.22)	1.50 (0.35)	1.80 (0.20)	1.56 (0.26)	1.52 (0.30)	2.16	0.88
	Chromaticity	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00
	Turbidity (NTU)	0.27 (0.089)	0.28 (0.060)	0.32 (0.091)	0.27 (0.068)	0.28 (0.074)	0.47	0.12
	Free residual chlorine (mg/L)	0.56 (0.00)	0.63 (0.01)	0.62 (0.06)	0.55 (0.06)	0.59 (0.03)	0.67	0.48
	Chlorine dose (mg/L)	1.45 (0.33)	1.53 (0.28)	1.50 (0.36)	1.43 (0.22)	1.47 (0.35)	1.57	1.38

[a]Spring: April, May, and June; Summer: July, August; Fall: September, October; Winter: November, December, January, February, and March.

Table 3
DBPs levels in drinking water system (standard deviations in parentheses)

DBPs (μg/L)	Raw water (N = 48)	Treated water (N = 48)				Distributed water (N = 72)			
	Maximum	Mean	Maximum	Minimum	Median	Mean	Maximum	Minimum	Median
TCM	BQL	8.91 (7.33)	42.80	2.90	6.70	15.25 (5.46)	29.10	6.80	14.60
CH	BQL	19.92 (5.74)	30.00	11.00	19.50	19.18 (5.48)	31.00	7.00	19.00
TCAA	BQL	9.00 (5.56)	27.00	2.00	7.50	12.68 (5.87)	24.00	3.00	13.00
DCAA	BQL	12.48 (5.67)	24.00	5.00	11.00	15.94 (6.96)	29.00	6.00	15.50

Table 1 and Fig. 1 for details on MQLs and sampling points, respectively.
BQL: Concentrations of DBPs were below method quantification limits (MQLs).

dosage in the drinking water system can be affected by the chlorine contact time. Relatively higher chlorine dosage in DWTP might cause higher chlorine residuals and significantly higher DBPs levels in the distribution system [11].

3.2. Occurrence of DBPs

As presented in Table 3 and Fig. S2, TCM, CH, TCAA, and DCAA were the main DBPs in both treated and distributed waters. The additional contact time of chlorine in the distribution system resulted in higher average DBPs levels of distributed water than that in treated water (Figs. S2a and b). CH was the predominant compound, constituting on average of 38.81% and 31.02% of the total DBPs in treated and distributed waters, respectively. CH has a risk of exceeding the standard (10.00 μg/L) in the drinking water system (Figs. S2a and b), with the highest level detected in the distribution system (31.00 μg/L; Table 3). Similar CH levels (up to 20.00 μg/L) have been reported in early Canadian DBPs occurrence surveys [12]. There are different precursor substances for TCM and CH [13]. Hydrophobicity and aromatic organics have higher TCM formation potentials [14], while hydrophilic low molecule weight organics are the main precursor substances of CH [3]. Fulvic acid (FA), a typical low-quality organic substance, has long existed in Mopanshan Reservoir. FA is considered as the main precursor of CH in DWPT. It is difficult to completely remove FA before chlorination [15]. Effective methods to control the formation of CH in the drinking water system will be discussed in this paper.

3.2.1. Temporal variations

The seasonal variation of each DBP is similar. The average levels of DBPs in treated and distributed waters were higher in fall and winter (Figs. 2a and b). Kruskal–Wallis *H*-test showed that the variations for DBPs in treated water with the season were significant ($P \leq 0.05$; Table S1). CH has a relatively higher risk of exceeding the standard (10 μg/L) in all seasons (Table 3). In treated water, CH reached a maximum of 30.00 μg/L in winter and a minimum of 11.00 μg/L in summer, the former was 2.7 times higher than the latter. In the distribution system, the highest concentration of CH was found during winter (29.75 μg/L at point DW 24) – about 1.36 times higher than that monitored during summer (21.90 μg/L at point DW 24). Higher precursor indicator loading (i.e., COD_{Mn}) and chromaticity were observed in raw and treated waters in the fall (as mentioned earlier). Unexpectedly, higher average levels of COD_{Mn} and chromaticity were not observed in raw and treated waters during winter (Table 2). In addition, considerable seasonal variations in water temperature seemed not strongly correlated to the seasonal occurrence and variation of DBPs. None of the parameters in Table 2 appeared to completely explain the seasonal patterns for DBPs.

CH is the predominant DBPs in each season (Figs. 2a and b). In treated water, CH accounted for the highest percentage of total DBPs in spring (46.20%) and the lowest in fall (34.88%). In distributed water, the highest percentage of CH in total DBPs was in summer (36.50%) and the lowest was in fall (22.04%). Water temperatures are higher in summer and fall (Table 2). The proportion of TCM in total DBPs in summer was significantly higher than in winter, which could attribute to the favorable chemical kinetics in warm water. CH as a precursor of TCM can be related to the increasing proportion of TCM in total DBPs [5]. Therefore, the generation of TCM while controlling the concentration of CH in the drinking water system needs additional attention.

Besides the mentioned seasonal variations, intra-seasonal variations in DBPs were studied. According to Fig. S3 and Table S2, although water temperature, COD_{Mn}, and chromaticity of the raw water varied considerably over the year, TCM was the only DBP of which statistically significant intra-seasonal variations in summer was observed in treated water (based on $P < 0.05$). The total DBPs level in August was higher than that in July (Figs. 3a and b). Considerable variations were observed for CH and total DBPs over a year in Figs. 3a and b. The intra-seasonal variations of CH and total DBPs in treated water were consistent with that observed at point DW 24 (Fig. 3a). Compared with DW 24, CH accounted for a higher proportion of total DBPs in treated water (Fig. 3b). This can be explained by the typical characteristics of raw water quality, operational parameters, the different precursors, formation mechanisms, and physicochemical properties of DBPs [16,17].

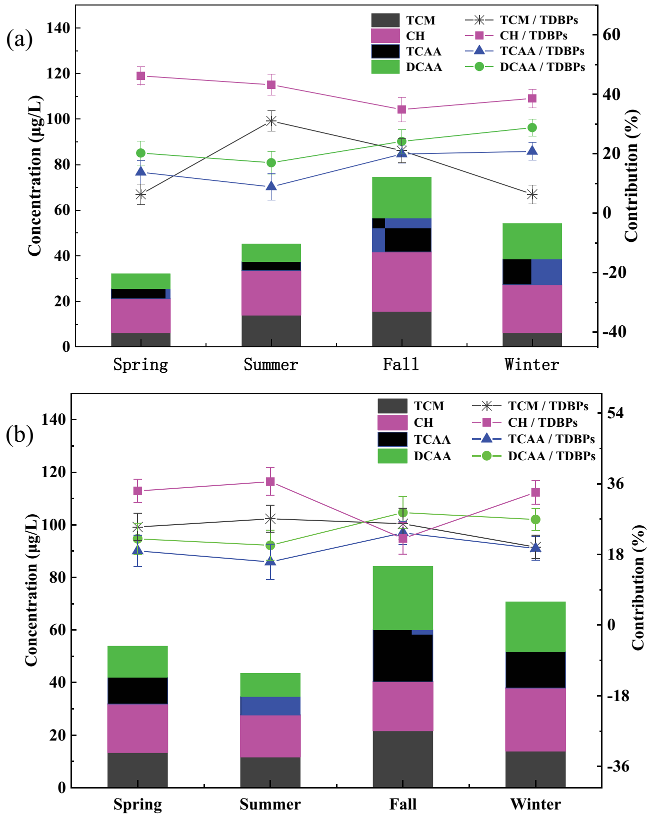

Fig. 2. Variations in average levels and percent contribution (wt/wt) of DBPs according to the season in (a) plant effluents and (b) distribution system ($N = 48$ for (a), $N = 72$ for (b); TDBPs = TCM + CH + TCAA + DCAA; Table 1 for details on analytes).

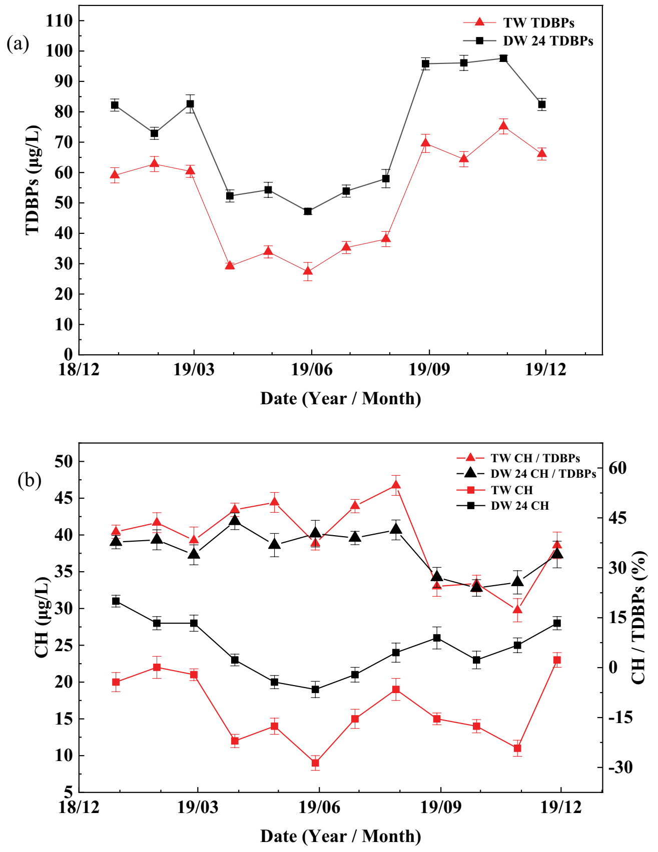

Fig. 3. Temporal variations of (a) CH, TDBPs and (b) the percent contribution (wt/wt) of CH in total DBPs at points TW and DW 24 (TDBPs = TCM + CH + TCAA + DCAA; Fig. 1 and Table 1 for details about each sampling point and analyte, respectively).

3.2.2. Spatial variations

The spatial variation pattern is similar for each DBP in the distribution system. As can be seen from Fig. 4, in the water distribution system, DBPs levels showed a monotonously increasing trend with the increase of residence time at the first 24 h, while with the depletion of chlorine residuals and DBPFPs, DBPs levels showed a decreasing or stabilizing trend. The CH spatial variation pattern in this paper was not totally consistent with the results from Gao et al. [3], who observed when chlorine residuals present in the distribution system, the level of fully chlorinated HALs (e.g., CH) will continue to increase monotonically, particularly after re-chlorination. In this distribution system, CH reached its maximum level at a certain point (DW 24) and then decayed, which was presumably caused by the transformation of CH into TCM in the presence of chlorine residuals [5]. CH accounted for the highest proportion of total DBPs in the first 24 h, while with the extension of residual chlorine contact time, CH/TDBPs levels gradually decreased to lower than TCM/TDBPs levels (Fig. 4). TCM/TDBPs levels continued to increase in the distribution system and finally overtook CH/TDBPs and TCAA/TDBPs levels (at point DW 72), TCAA/TDBPs levels in treated water were shown higher than DCAA/TDBPs levels (Fig. 4). Therefore, CH and TCAA should be two of the precursors of TCM in this distribution system.

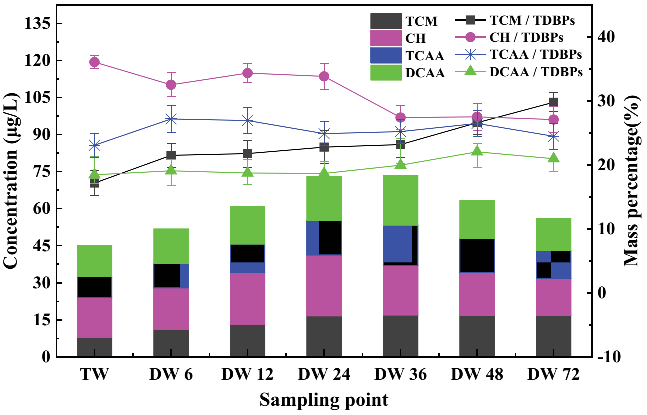

Fig. 4. Variations in average levels and percent contribution (wt/wt) of DBPs according to increasing water residence times in drinking water (treated and distributed waters) (N = 84; TDBPs = TCM + CH + TCAA + DCAA; Fig. 1 and Table 1 for details about each sampling point and analytes, respectively).

In summary, the most investigated HALs in drinking water, CH, continued to form in the distribution system when free chlorine residual was presented in the distribution system. As CH was formed, it simultaneously undergoes degradation or transformation to generate other DBPs (e.g., TCM). The spatial variation pattern of each DBP in this paper was not influenced by seasons (Figs. S4a–d). Each DBP level reached its maximum at the point of DW 24 or DW 36 (Fig. 4). CH level in the distribution system increased about 1.5 times between point TW and point DW 24. Except for TCM, the concentration of each DBP at DW 72 was approximately equal to that at TW. TCM level at DW 72 was 2.2 times higher than that at TW. Additional attention was needed for the sites located in the middle of the network to control excessive CH levels in this system [18].

3.3. Correlations of DBPs concentrations with other parameters

As shown in Table 4, Spearman correlation coefficients (r) were calculated between the levels of DBPs measured in the treated water and some important parameters (COD_{Mn}, chromaticity, water temperature, turbidity measured in raw water, and disinfectant dosages applied for chlorination). In general, COD_{Mn} and chromaticity were the main factors affecting the total occurrence of DBPs in treated water (r = 0.517, 0.458, respectively). They also had a significant impact on CH occurrence (r = 0.421, 0.433, respectively). Chlorine treatment can increase CH precursors by oxidizing

Table 4
Spearman correlation coefficients (r) between DBPs levels and water quality or operational parameters for DWTP (TCM, CH, TCAA, and DCAA at TW, chromaticity, temperature, COD_{Mn}, and turbidity at RW) during all sampling campaigns (N = 48) (Fig. 1 for details about each sampling point)

Parameters	TCM	CH	TCAA	DCAA	Total DBPs
TCM	1.000				
CH	N.S.	1.000			
TCAA	N.S.	0.358*	1.000		
DCAA	N.S.	0.482**	0.910**	1.000	
Total DBPs	0.345*	0.741**	0.796**	0.843**	1.000
COD_{Mn}	N.S.	0.421**	0.320*	0.376*	0.517*
Chromaticity	N.S.	0.433**	N.S.	0.367*	0.458**
Water temperature	0.525**	N.S.	N.S.	N.S.	N.S.
Turbidity	N.S.	N.S.	N.S.	N.S.	N.S.
Chlorine dose	N.S.	N.S.	N.S.	N.S.	N.S.

see Table 1 for details on analytes.
N.S.: Not significant.
*Correlation was significant using a significance of the level of 0.05 (2-tailed).
**Correlation was significant using a significance of the level of 0.01 (2-tailed).

NOM in water [19]. Unexpectedly, there was no significant correlation between chlorine dosage and CH occurrence in this study, nor was the water temperature and CH occurrence. FA is one of the precursors of CH and it is also the main chromogenic substance in raw water [15]. It is suggested that the quality (e.g., speciation) of the DBPFPs is more likely to explain the formation of CH in drinking water than the quantity (e.g., COD_{Mn}) [20], therefore, a moderate correlation between COD_{Mn} and CH occurrence can be justified. In a full-scale study, it is necessary to use substituted precursors with different characteristics (e.g., hydrophobic or hydrophilic fractions and molecular magnitude) to show correlations with the formation of DBPs [21]. Correlations between each DBP in the treated water are presented in Table 4. It should be noted that sampling points in the distribution system were not included in this analysis because of the complex hydraulic conditions of the system. The strongest positive correlation between TCAA and DCAA (i.e., $r = 0.910$) was obtained in treated water. There was no significant correlation between TCM and CH, only moderate correlations (i.e., $r < 0.500$) were obtained between CH and TCAA, CH, and DCAA. These observations suggested that TCM cannot serve as a good indicator for CH generation in treated water, which was not consistent with a formal study [22]. The reason for this discrepancy could be related to the different precursors of TCM and CH [13].

Fig. 5 shows the temporal variations of total DBPs and TCM in treated water, as well as the monthly average precipitation of Harbin. The total DBPs concentration showed a considerable variation from January 2016 to December 2019. Several peaks and troughs in total DBPs and TCM concentrations coincided with heavy rainfall events. A moderate correlation was found between total DBPs and rainfall (lag 2 months, $r = 0.444$, $P < 0.01$). TCM in treated water also had a moderate correlation with rainfall (lag 2 months, $r = 0.487$, $P < 0.01$), and this result was consistent with the study which had shown a moderate correlation between monthly TCM concentration and rainfall (lag 1 month, $r < 0.600$) for the Sydney/Illawarra [1]. Both catchment runoff and flow patterns have significant effects on the concentration and characteristics of organics in river waters [23]. However, the storage of large volumes of water in the reservoir (e.g., Mopanshan Reservoir) and the long-distance hydraulic transportation (Mopanshan Reservoir is 180 km far away from the DWPT) enable the mixture of influent waters and the stabilization of water quality. This might lead to a delayed effect of rainfall on TCM and total DBPs in the treated water. Different drinking water treatment plants could have different lag times due to different raw water transportation conditions [24]. Precipitation (lag 2 months) does not correlate with the monthly average concentration of CH, TCAA, and DCAA in the treated water, and this might be related to the different precursors of each DBP [3].

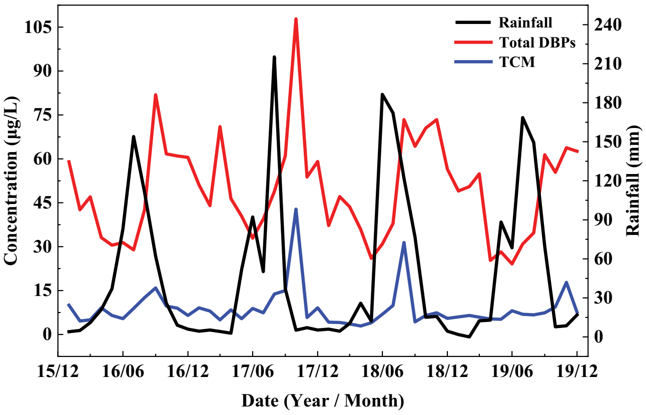

Fig. 5. Temporal variation in Harbin monthly total DBPs and TCM concentration and monthly rainfall ($N = 48$).

3.4. *Effective methods to control the formation of CH in the drinking water system*

CH has a high risk of exceeding the standard (10 μg/L) in the drinking water system. Compared to pH, water temperature, turbidity and chlorine dosage, COD_{Mn}, and chromaticity appeared to be the most influential factors for CH formation in the raw water (as mentioned above). The quality (e.g., speciation) of the DBPFPs is more likely to explain the formation of DBPs in drinking water than the quantity so that the composition and concentration of NOM should be considered when controlling the formation of CH in the drinking water system. Different types of water samples were selected in this paper (according to section 2.4 (Bench-scale hydrolysis and chlorine contact disinfection experiments)) to conduct the CH hydrolysis experiment. CH can decompose to produce TCM in neutral, acidic, and alkaline solutions [5], while in the experimental water samples, the species and concentrations of organic substances have no significant effect on the hydrolysis of CH ($P > 0.05$) (Fig. S5).

Fig. 6 shows the changes of TCM and CH over time in the four water samples (according to section 2.4 (Bench-scale hydrolysis and chlorine contact disinfection experiments)) after using 1.5 mg/L sodium hypochlorite. In the bench-scale chlorine contact disinfection experiment, the formation pattern of CH and TCM in four types of water samples was different. CH and TCM levels increased continuously with contact time in the presence of chlorine residuals in the water. In general, compared with HWTP water samples, DWTP water samples had a higher CH level. The average concentration of CH in sand filtered water in DWTP was 3 times that of HWTP. The concentration of TCM and CH can be significantly controlled by GAC secondary filtration. After GAC secondary filtration, for the sand filtered water samples in DWTP, the concentrations of TCM and CH decreased by 32.45% and 32.78%, respectively. While for the sand filtered water samples in HWTP, the concentration of TCM decreased by 29.46% and CH was below MQLs.

GAC secondary filtration can intercept part of organic matter in water, resulting in the reduction of DBPFPs. So that DBPFPs of raw water can be controlled to achieve the purpose of controlling the level of CH in the drinking water system [25]. It is important to note that with the extension of contact time, there were increasing trends for TCM and CH levels which did not slow down. Therefore, considering the health of the residents, disinfection patterns adjustment (e.g., secondary chlorination strategy) is an effective

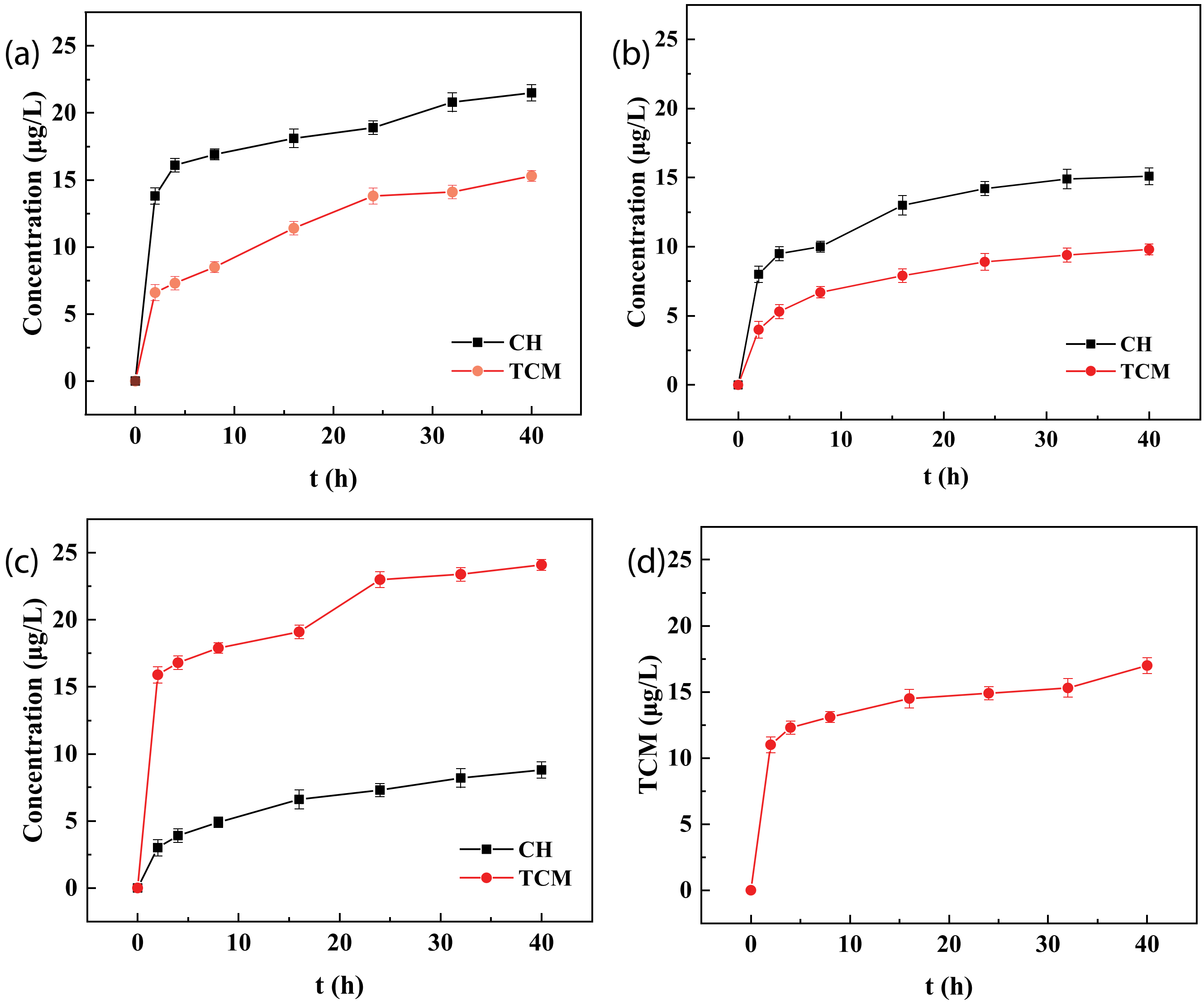

Fig. 6. Temporal variations of CH levels in different types of water samples after chlorination: (a) DWTP sand filter effluent, (b) DWTP GAC filter effluent, (c) HWTP sand filter effluent, (d) HWTP GAC filter effluent; sodium hypochlorite = 1.50 mg/L; $T = 15°C$; pH = 6.9.

strategy to reduce DBPs levels in the drinking water system, besides controlling DBPFPs in raw water by secondary filtration, enhanced coagulation, usage of disinfectants with different disinfection principles and chlorine dosages control [25].

4. Conclusions

In this study, a conventional chlorine disinfection strategy was applied in the drinking water treatment system. DBPs were monitored for 4 y at the plant effluents. A 1 y survey was carried in the distribution system. All the above can provide the following key conclusions:

Statistically significant differences ($P < 0.05$) for DBPs were observed among four seasons in DWPT, with the higher average levels of each DBP (TCM, CH, TCAA, and DCAA) occurred during fall and winter. TCM was the only DBP of which statistically significant intra-seasonal variations in summer were observed in treated water (based on $P < 0.05$).

The spatial patterns for DBPs were not affected by seasons, DBPs concentrations increased monotonously and reached the maximum at the point of DW 24 or DW 36 in the water distribution system, and then decreased or tended to be stable. CH has a risk of exceeding the standard in treated and distributed waters. CH levels in the distribution system increased about 1.5 times between TW and DW 24 and then decreased.

For the 4 y survey, only COD_{Mn} and chromaticity have moderate correlations with total DBPs (r = 0.517, 0.458, respectively), no significant correlation was found between chlorine dosage and CH occurrence in this study, nor did the water temperature and CH occurrence. Only TCM concentration had a moderate correlation with rainfall (lag 2 months, $r = 0.487$), which had a delayed effect on TCM levels in treated water in this paper. TCM could not serve as an indicator for CH generation in DWPT, while moderate correlations (i.e., $r < 0.500$) were obtained between CH and haloacetic acid (TCAA and DCAA) in DWPT.

To understand and control the presence of CH in water, various future research directions need to be identified:

The sites located at the distribution system need additional attention to control DBPs formation. It is necessary to focus on the generation of TCM while controlling the concentration of CH in the drinking water system.

Since the seasonal variation of COD_{Mn} in raw water did not change dramatically in this paper, the species composition and molecular magnitude of NOM in raw water should be identified in future full-scale occurrence studies.

As the extension of disinfectant and the water contact time, there were increase trends for CH and TCM levels. Therefore, disinfection patterns adjustment (e.g., secondary chlorination strategy) can be considered as an effective strategy to reduce DBPs levels in the drinking water system.

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Supplementary information

Table S1
Inter-seasonal differences of DBPs in DWTP ($N = 48$)

Parameters	Sample groups (season)	TCM	CH	TCAA	DCAA	Total DBPs
P	(Spring/summer/fall/winter)	**	**	**	**	**
	Spring/summer	**	N.D.	N.D.	N.D.	N.D.
	Spring/fall	N.D.	**	**	**	**
	Spring/winter	N.D.	**	**	**	**
	Summer/fall	N.D.	N.D.	**	**	N.D.
	Summer/winter	**	N.D.	**	**	N.D.
	Fall/winter	N.D.	N.D.	N.D.	N.D.	N.D.
Mean (μg/L)	Spring	6.34	14.83	4.42	6.50	32.09
	Summer	14.00	19.50	4.00	7.67	45.17
	Fall	15.70	26.00	14.83	18.00	74.53
	Winter	6.40	20.50	11.11	15.39	53.40

**Significant at $P < 0.05$, there was a significant difference among (between) sample groups at $\alpha = 0.05$ (*P*: sig. (2-tailed)).
N.D.: There was no significant difference between sample groups.

Table S2
Intra-seasonal differences of DBPs in DWTP ($N = 48$)

Parameters	Season	Sample groups (month)	TCM	CH	TCAA	DCAA	Total DBPs
P	Spring	4, 5, 6	N.D.	N.D.	N.D.	N.D.	N.D.
	Summer	7, 8	**	N.D.	N.D.	N.D.	**
	Fall	9, 10	N.D.	N.D.	N.D.	N.D.	N.D.
	Winter	11, 12, 1, 2, 3	N.D.	N.D.	N.D.	N.D.	N.D.
Mean (μg/L)	Summer	7	8.73	15.33	4.33	7.00	35.40
		8	19.27	23.67	3.67	8.33	54.93

N.D.: There was no significant difference among (between) sample groups.
**Significant at $P < 0.05$, there was a significant difference between sample groups at $\alpha = 0.05$ (*P*: sig. (2-tailed)).

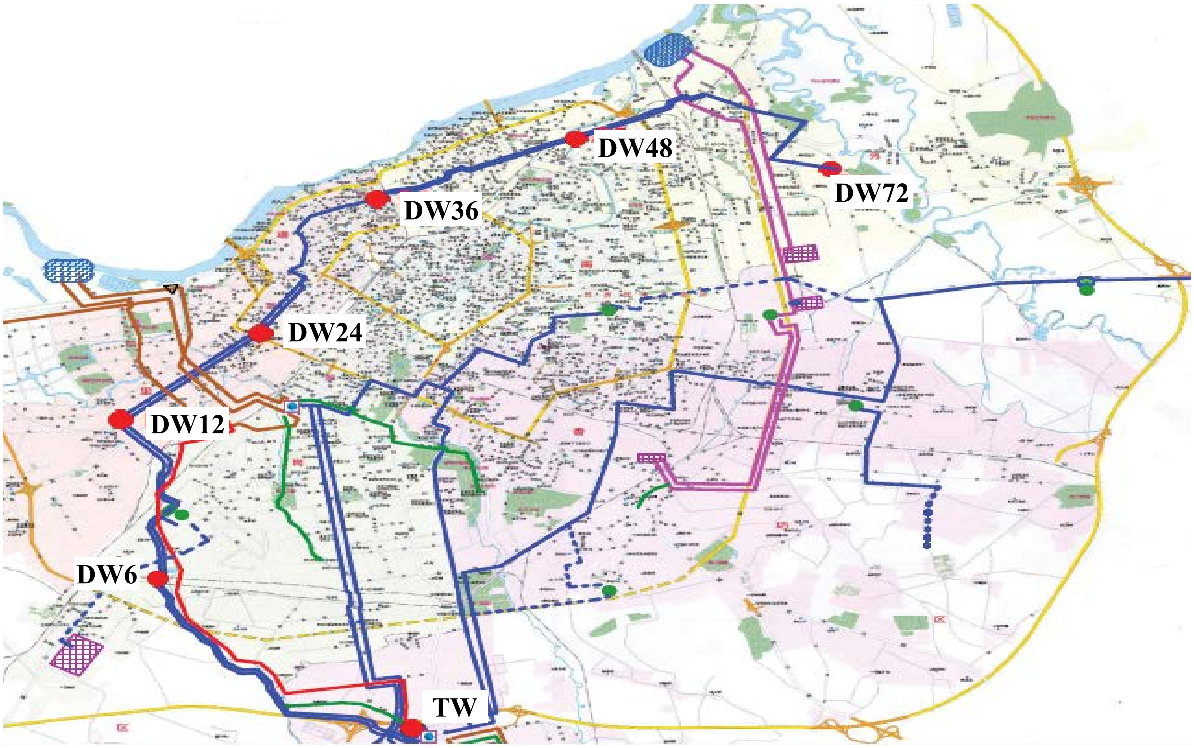

Fig. S1. Sampling points along with the distribution system.

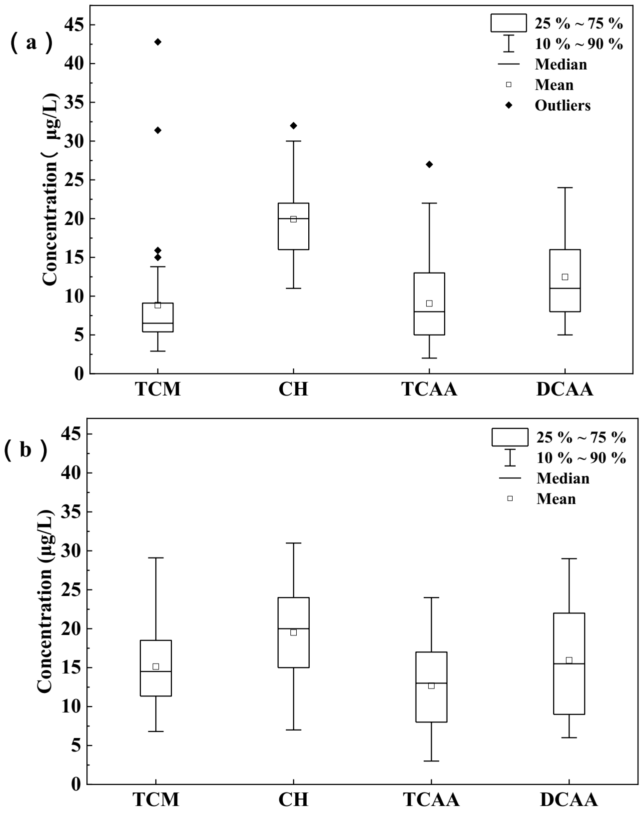

Fig. S2. Concentrations of DBPs in (a) plant effluents and (b) distribution system (N = 48 for (a), N = 72 for (b); Table 1 for details on analytes).

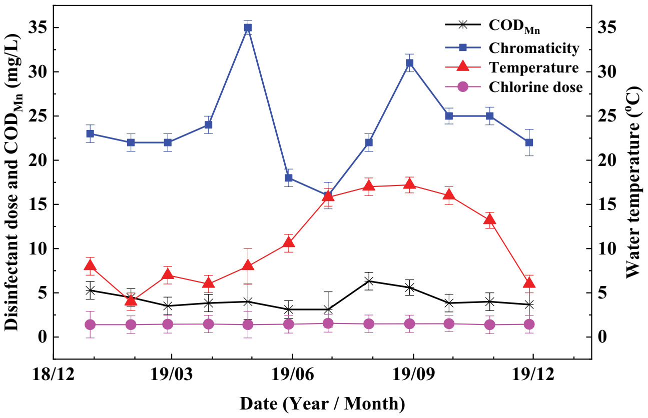

Fig. S3. Temporal variations in the physico-chemical quality of raw water and operational parameters during the studied period in DWPT (Fig. 1 for details about each sampling point).

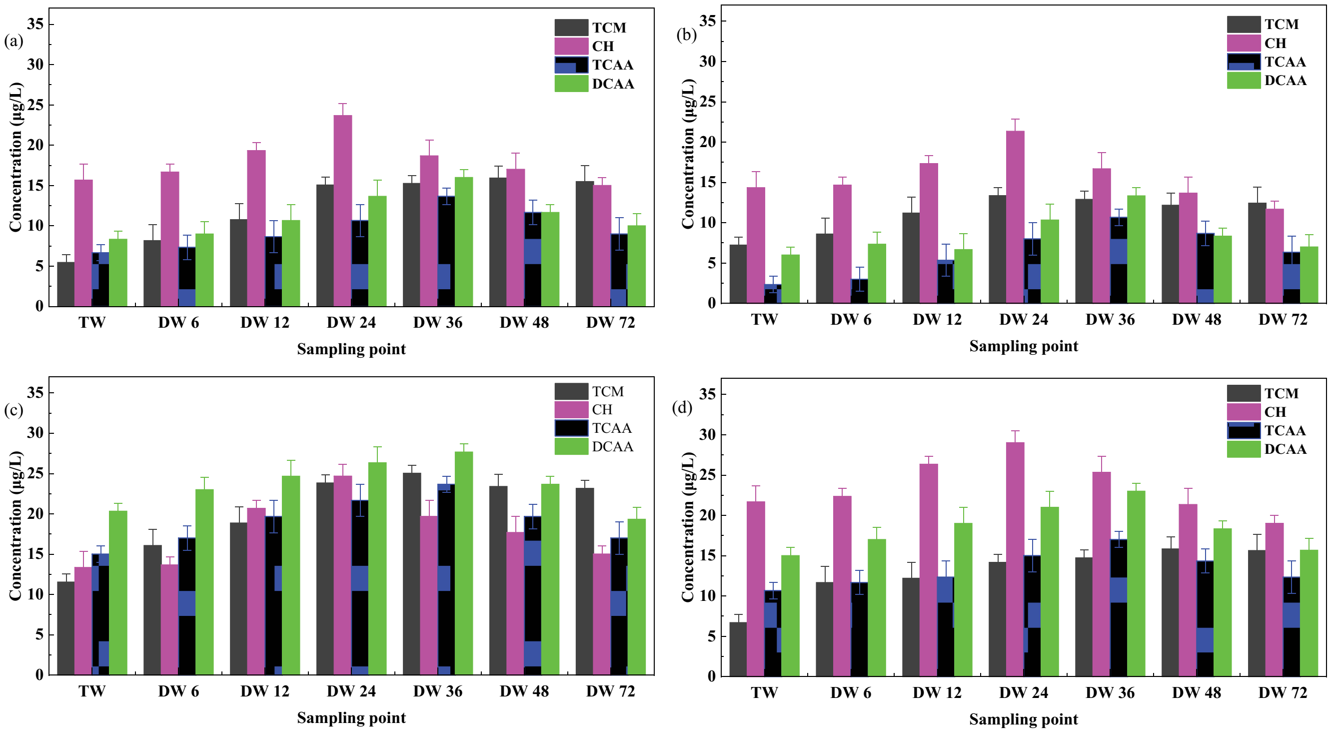

Fig. S4. Variations in average levels of DBPs according to increasing water residence times in drinking water (treated and distributed waters) in (a) spring, (b) summer, (c) fall, and (d) winter ($N = 21$ for (a), $N = 14$ for (b), $N = 14$ for (c), and $N = 35$ for (d); Fig. 1 and Table 1 for details about each sampling point and analytes, respectively).

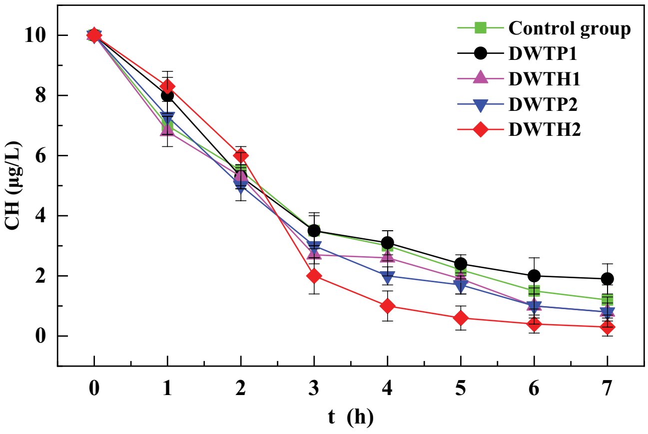

Fig. S5. Temporal variations of CH levels in different types of water samples (water-bath heating $T = 40$°C; pH = 6.9; DWTP1: DWTP sand filter effluent, DWTP2: DWTP GAC filter effluent, DWTP1: DWTP sand filter effluent, DWTP2: DWTP GAC filter effluent).